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Biogeochemical reduction of U(VI) in a low-level radioactive waste repository

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The Drigg disposal site in Cumbria is the principal facility in the UK for the disposal of low-level radioactive waste (LLW). As part of an ongoing research programme in support of Drigg post-closure safety case, this study focuses on the evolution of stable element biogeochemistry within LLW waste and the effect this has on uranium solubility. Anaerobic batch culture experiments using a Drigg synthetic leachate at circumneutral pH were inoculated with an indigenous microbial culture from the Drigg LLW repository. The indigenous microorganisms showed evidence of denitrification, followed by rapid reduction of Fe(III) to Fe(II) coupled to the oxidation of acetate. Reduction of SO_4^{2-} to HS^- occurred after denitrification and Fe(III) reduction, with the formation of an amorphous FeS phase. When U(VI) was added (126 µM), 93.4 ± 0.7% was reduced to U(IV) after denitrification but prior to Fe(III) reduction. Sulfate reduction occurred in the same period as U(VI) reduction. When SO_4^{2-} was omitted, U(VI) and Fe(III) reduction were affected (32.5 ±4.8% of initial U(VI) reduced). However, when sulfate was available but dissimilatory SO_4^{2-} reduction was inhibited, Drigg culture was able to significantly reduce U(VI) (75 ± 4.2%) prior to the reduction of Fe(III). This study indicates that microbial metabolism influences metal ion solubility in low-level waste and suggests that sulfate may influence the reduction of U(VI) to U(IV).

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Technetium remobilisation during the reoxidation of Tc-radiolabeled sediments

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Technetium-99 is a long-lived (half life 2.1 x 10^5 years) β-emitting radionuclide formed in high yield during nuclear fission and is a key radionuclide associated with radioactive wastes. In reducing environments Tc is bound to sediments and immobilised as Tc(IV). In dynamic environments Tc-radiolabeled sediments may be prone resuspension in oxygenated waters resulting in aerobic oxidation and release of Tc. In contrast, nitrate-rich nuclear waste streams may cause anaerobic oxidation in groundwater plumes. Significant amounts of Tc where found to be remobilised when sediments are exposed to oxygen, but although aqueous nitrate was found to totally oxidise sediment bound Fe(II), only a small amount of Tc was remobilised.

Aerobic reoxidation with oxygenated water

Tc radiolabeled iron and sulphate reducing sediments were exposed to air in continually agitated flasks. Both Fe(II) and sulphide were rapidly oxidised and significant Tc remobilisation occurred. In iron-reducing sediments, 42% Tc was remobilised after 8 days, and 64% after 66 days. In sulphate-reducing sediments Tc remobilisation was slower with just 17% Tc remobilised after 9 days. When sediments were sterilised (120ºC) prior to oxidation, only 25% Tc remobised after 66 days, indicating that reoxidation may be enhanced by microbial action.

Anaerobic reoxidation with deoxygenated nitrate

Nitrate additions (0.6, 6, 20, 60, 250 mM) were made to Tc radiolabeled iron- and sulphate-reducing sediment microcosms. Nitrate reduction coupled to the oxidation of both Fe(II) and sulphide was stimulated, and nitrite accumulated in porewaters. Despite the dramatic changes in iron and sulphide geochemistry, only minor amounts of Tc were remobilised. In iron-reducing microcosms 8% Tc was remobilised after 62 days and in sulphate-reducing microcosms only 2.2% Tc was remobilised after 60 days. When sediments were sterilised (120ºC) prior to nitrate addition; nitrate reduction, Fe(II) oxidation and Tc remobilisation were completely inhibited. In unsterilisaed experiments where nitrate concentrations were less than the sediment bound Fe(II) (15-30 mM), Tc remobilisation was also inhibited.